OBSERVATIONS ON THE MESOMORPHIC STATE WITH SPECIAL REFERENCE TO CARBON

BY
ALFRED CARL ECKERT, JR.
B.S., Wheaton College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1945

URBANA, ILLINOIS
1945

OBSERVATIONS ON THE MESOMORPHIC STATE WITH SPECIAL REFERENCE TO CARBON

BY
ALFRED CARL ECKERT, JR.
B.S., Wheaton College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1945

URBANA, ILLINOIS
1945

Acknowledgment

The author wishes here to express his deep appreciation to Professor G. L. Clark under whose supervision this investigation was conducted. The work was greatly aided by his wise, patient counsel, and his personal, zealous interest. The author also appreciates the help from his associates in the laboratory resulting from the pleasant, congenial atmosphere which they created and maintained. He further expresses his appreciation to Mr. Merton Studebaker of the Carbon Section of the War Production Board for his unusual interest in supplying materials and data which made this study possible.

A special debt of gratitude is due those in authority in the Graduate School of the University of Illinois, in the University of Chicago, and the Carbide and Carbon Chemicals Corporation, whose excellent, willing cooperation made the completion of this work possible.

The author wishes further to express his appreciation to his parents and to his wife for their prayers, inspiration, constant encouragement, and material help essential to the preparation and completion of the manuscript. They considered the task one of their own.

OBSERVATIONS ON THE MESOMORPHIC STATE WITH SPECIAL REFERENCE TO CARBON

Introduction

This investigation was undertaken, in one aspect, at the specific request of the War Production Board for the purpose of organizing and coordinating the available information on carbon blacks. This information has heretofore been so scattered, contradictory, and controversial, that the task of classification of carbon blacks remained extremely difficult. No attempt has previously been made to make such a classification with regard to their crystalline states or structural stages, of which many have been observed. Knowledge has been so disorganized that no practical system of nomenclature is being used. As a tool for this badly needed classification and organization the x-ray diffraction method is the most promising and significant because by its use each black gives a characteristic pattern which can be quantitatively examined.

Throughout this investigation two lines of emphasis have been made. First, to satisfy the request of the War Production Board, and to make the investigation of popular value, the practical point of view has been emphasized. Second, to make the investigation of academic value, the theoretical point of view has been emphasized.

Carbon, in the elementary form, holds great interest for the academic investigator in that it exists in three allotropic structural forms. One of these forms, diamond, is distinct from the others, but graphite and "amorphous" carbon have many close structural relationships. Between graphite and the most amorphous carbon available there are numerous products which exist in the mesomorphic state, which is defined as that state in which matter exhibits an amount of orderly arrangement of component particles, but does not exhibit the complete orderly structure of a crystalline material. The x-ray diffraction powder pattern of matter in the mesomorphic state consists of one or more halos. For convenience in this writing, the term "amorphous carbon"

is used to designate any carbon which is not definitely diamond or graphite. Carbon thus gives an excellent example for a study of the mesomorphic state.

Experimental

This study consists of the examination of x-ray diffraction powder patterns of various samples of carbon and graphite. These patterns are examined from six points of view, each one revealing certain facts concerning the structural characteristics of the sample giving the pattern. The number and type of interferences on the pattern indicate the degree of crystallinity. The positions of the interferences give a means of calculating interplanar spacings, and thus their variation from one sample to another. The shape or symmetry of the interferences reveal whether the interference was caused by structural elements which have a two-dimensional spatial arrangement or by elements which have a three-dimensional arrangement. The breadth of interferences gives a measure of particle size. The relative intensities of the interferences on a pattern give indications of the crystal development of distortion. Scattering of x-rays at small angles gives some information concerning the existence of clusters of particles or of voids between particles. As these data are collected from the various patterns an attempt is made to correlate them with known properties and histories of the various samples.

Results

Practical application of this study has been made in several directions. By the above mentioned correlations it is suggested that the x-ray pattern of a given carbon may be used to reveal the degree and direction of graphitization of the carbon and thus predict its adaptability to a given use. Patterns of synthetic mixtures of amorphous carbon and graphite make possible the suggestion of the use of such patterns for a determination of graphitic carbon in the presence of amorphous carbon. It is also suggested that a nomenclature for carbon blacks be based on their diffraction patterns. Thus, from the data mentioned above several conclusions are drawn.

Among more than fifty different samples of commercial and experimental carbons, graphitic acids, and graphites no two gave identical x-ray diffraction patterns. As a result of these characteristic patterns a practical, significant, inclusive system of designation for these materials is presented.

Some correlation is demonstrated between ease of processing of channel carbons with rubber and their structural characteristics as revealed by these patterns.

The scattering of x-rays at small angles increases with temperature of heat treatment for equal lengths of time. This indicates a growth of clusters of particles.

Patterns of carbons heat-treated at high temperatures show evidence of change in structural properties independently of each other. The value of each lattice parameter varies independently of the other, and the size of the particle in each principal direction varies independently of the size in the other direction. Particle size varies independently of lattice parameters.

The various patterns show the existence of carbon in many different mesomorphic states, each state being defined by a set of values for the lattice parameters and particle size.

Comparisons of patterns of various starting materials and graphitic acids derived therefrom show independently variable dimensions in this class of substances. Inspection of patterns of various natural and artificial graphites reveals marked difference in the structural properties of these substances.

Patterns of mixtures of graphite and an amorphous carbon indicate the possibility of the development of two practical methods for the determination of graphite in the presence of amorphous carbon. These methods are similar to common methods employed in quantitative spectrographic analysis.

The data collected here confirm the difference between particle diameters determined from electron microscope photographs and the particle dimensions derived from x-ray data. The electron microscope diameters are of a much greater order of magnitude than those determined from x-ray data and bear little correlation to them. They are explained as the diameters of aggregates of the smaller primary particles detected by the x-ray method.

Bibliography

1. Clark, G. L., and Rhodes, H. D., Ind. Eng. Chem. Anal. Ed. 12, 66-71 (1940).
2. Warren, B. E., and Biscoe, J., J. Applied Phys. 13, 364-71 (1942).
3. Rhodes, H. D., Thesis, Doctor of Philosophy, University of Illinois, Urbana, 1939.
4. Warren, B. E., J. Chem. Phys. 2, 551 (1934).
5. Warren, B. E., Phys. Rev. 59, 693 (1941).
6. Guinier, M. A., Thesis, Doctor of Philosophy, University of Paris, Paris, 1939.
7. Cohan, L. H., and Mackey, J. F., Ind. Eng. Chem. 35, 806 (1943).
8. Hoffman, U., and Wilm, D., Z. Electrochem. 42, 504 (1936).

Vita

The author was born in Newark, New Jersey, on June 12, 1920. He received his elementary education in the public schools of Chatham, Westfield, and Maplewood, New Jersey, and in private schools in Madrid, Spain; junior high school and ninth grade in El Dorado, Kansas; tenth grade in Fremont High School, Oakland, California; eleventh grade in Oak Park, Illinois; graduated from Wheaton College Academy, Wheaton, Illinois, in June, 1937. He entered Wheaton College, Wheaton, Illinois, in September, 1937, serving four semesters and one summer as assistant in the chemistry laboratory and receiving from that institution the degree of Bachelor of Science with honor, in June, 1941.

During the summer after graduation he taught courses in Wheaton College and Wheaton College Academy and during another summer he taught chemistry courses in Wheaton College.

He held a teaching assistantship in the Chemistry Department of the University of Illinois during his enrollment in the Graduate School there from September, 1941, to May, 1944, when he was granted leave to serve as a junior chemist at the University of Chicago with permission to write his thesis in absentia.

He is a member of Sigma Xi, Sigma Pi Sigma, Alpha Delta, and the American Chemical Society.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549820_0068